agents were carried out under the same experimental conditions. Details of the procedure are described for the reaction of diallyl ether with *t*-butylmagnesium bromide. One and two-tenths moles of *t*-butylmagnesium bromide (prepared in diethyl ether) was placed into a flask. The first of two tubes connected in series was attached to the flask through the head of a condenser. The first tube was surrounded by a frozen carbon tetrachloride bath; the second by a Dry Ice–chloroform-bath (−45°). The outlet to the second tube was attached to a vacuum line equipped with three traps; the first two were surrounded by Dry Ice–chloroform and the third by liquid nitrogen. The reaction flask was flushed with dry nitrogen. Stirring was started and one mole (98 g.) of diallyl ether dissolved in an equal volume of dry diethyl ether was added dropwise. The reaction was heated 2 hours and then hydrolyzed with saturated ammonium chloride. The ether layer of the hydrolyzed mixture was separated and the aqueous layer extracted continuously. The ether extracts were combined and dried over anhydrous magnesium sulfate. Removal of the ether and fractional distillation of the residue through a Todd column (60 theoretical plates) gave 4,4-dimethyl-1-pentene (7.5%), b.p. 72–74° (737 mm.); allyl alcohol (56%), b.p. 87–89° (737 mm.); and *t*-butoxy-1-propene (5%), b.p. 185–187° (746 mm.).

The gaseous hydrocarbon was trapped in the third tube on the vacuum line and identified as propylene. Its molecular weight was determined by the Regnault method. The observed molecular weight (average of five determinations) was 43. The gaseous hydrocarbon gave positive tests for unsaturation when bubbled into bromine–carbon tetrachloride and potassium permanganate solutions.

Physical constants, yields and identification information for reaction products obtained from the several reactions are shown in Table I.

Preparation of 1,2-Dibromoheptane.—A solution of 2 g. of 1-heptene in 15 ml. of carbon tetrachloride was chilled in an ice–water-bath. To the chilled solution was added dropwise a dilute solution of bromine in carbon tetrachloride; the addition was continued until a light brown color persisted. The reaction mixture was allowed to warm to room temperature, and the solvent removed by distillation. Distillation of the residue gave 1,2-dibromoheptane, b.p. 120° (28 mm.). Bromine analysis of the dibromide was made according to the Pregl catalytic combustion method.[5]

Anal. Calcd. for $C_7H_{14}Br_2$: Br, 62.01. Found: Br, 62.31.

Identification of Unsaturated Products.—The olefinic hydrocarbons, except 1-heptene, were identified by ozonization. One- to four-gram samples of the olefins were dissolved in 50–75 ml. of petroleum ether or *n*-hexane, and the solution treated with an oxygen–ozone stream for 5–12 hours. The solvent was then removed by distillation. The ozonide was then added dropwise to a warm mixture of zinc dust and water contained in a flask. A trap containing 2,4-dinitrophenylhydrazine reagent was attached to the flask through the head of a condenser. After addition of the ozonide, the reaction mixture was heated 30 minutes and cooled. The mixture was filtered and the filtrate extracted several times with small portions of diethyl ether. The extracts were combined, dried, and the solvent removed. Distillation of the residue separated the liquid aldehydes, which were identified by preparation of their 2,4-dinitrophenylhydrazones. The formaldehyde which formed during decomposition of the ozonides of 4,4-dimethyl-1-pentene and allylbenzene was collected as the 2,4-dinitrophenylhydrazone in the hydrazine trap.

Identification of γ-Phenyl γ′-Methyldiallyl Ether.—The observed physical constants of this ether are: b.p. 120–123° (6 mm.), $d^{20}{}_4$ 0.982, $n^{20}{}_D$ 1.5418; MR_D 59.34 (calcd.), 60.37 (found). The compound gave positive tests for unsaturation and for the ether linkage. A 4-g. sample was dissolved in 150 ml. of petroleum ether and treated with ozone as described above. Ozonolysis products isolated were benzaldehyde and acetaldehyde; melting points of their 2,4-dinitrophenylhydrazones were 237° and 168°, respectively; reported melting points are 168° and 237° by footnote *a* of Table I.

Anal. Calcd. for $C_{13}H_{10}N_4O_4$: N, 19.60. Found: N, 19.90. Calcd. for $C_8H_8N_4O_4$: N, 25.00, Found: N, 25.70.

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[5] A. Steyermark, "Quantitative Organic Microanalysis," The Blakiston Co., New York, N. Y., 1951, p. 184.

NASHVILLE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Rearrangements of Aryl Sulfones. I. The Metalation and Rearrangement of Mesityl Phenyl Sulfone[1]

BY WILLIAM E. TRUCE, WILLIAM J. RAY, JR., OSCAR L. NORMAN AND DANIEL B. EICKEMEYER

RECEIVED MARCH 13, 1958

The *n*-butyllithium-induced rearrangement of mesityl phenyl sulfone (I) to 2-benzyl-4,6-dimethylbenzenesulfinic acid (III) is reported. A mechanism is proposed for the rearrangement analogous to the base-catalyzed Smiles rearrangement.[2]

During the course of an investigation of the substituent group effect in the metalation of diaryl sulfones[3a,b] the reaction of *n*-butyllithium with mesityl phenyl sulfone (I) was studied. When a solution of sulfone I in refluxing ether was treated with a slight excess of *n*-butyllithium, the initially deep red solution became light orange and a flocculent precipitate developed over a period of a few minutes. On hydrolysis, essentially the entire product was base soluble, and, on acidifying the resulting basic solution, a solid, almost colorless acid, having a neutral equivalent equal to the molecular weight of the starting sulfone, was obtained in 98% yield.

An intramolecular rearrangement, similar to the base-induced Smiles rearrangement[2] of 2-hydroxy-2′-nitrodiphenyl sulfone to 2-(2-nitrophenoxy)-benzenesulfinic acid, and involving metalation of I at an *o*-methyl group, as outlined, is suggested. The Smiles rearrangement[2] also includes the intramolecular displacement of the arylsulfonyl group of an appropriate sulfone by $-S^{\ominus}$ and –NHR (R = –H, –COR′, $-SO_2Ar$). However, our example appears to be the first such displacement involving a carbanion or its equivalent.

An indication of the structure of III was first obtained by oxidation and subsequent desulfonation to 3,5-dimethyldiphenylmethane. This hydrocarbon was synthesized by the Wolff–Kishner reduction of 3,5-dimethylbenzophenone, and was

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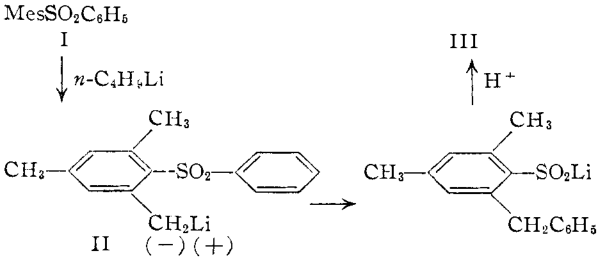
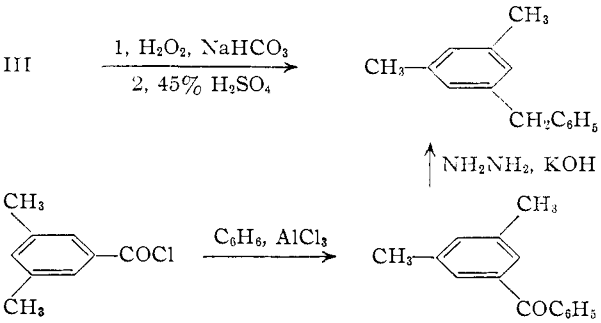
[1] This paper was presented in part at the Symposium on Aromatic Substitution, American Chemical Society Meeting, Atlantic City, N. J., September, 1956. Abstracted in part from the Ph.D. Theses of William J. Ray, Jr., Oscar L. Norman and Daniel B. Eickemeyer.

[2] J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 362 (1951).

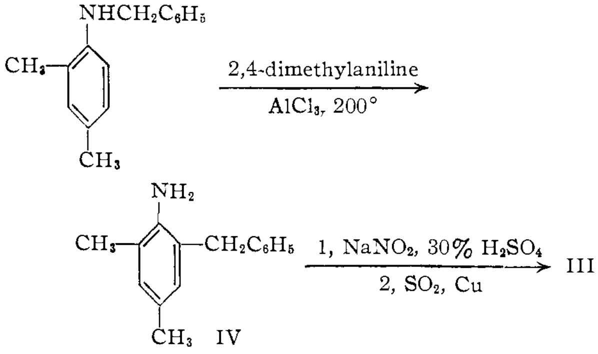
[3] (a) W. E. Truce and M. F. Amos, THIS JOURNAL, **73**, 3013 (1951); (b) W. E. Truce and O. Norman, *ibid.*, **75**, 6023 (1953).



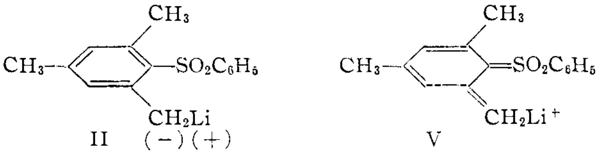
identical in refractive index and infrared spectrum to the hydrocarbon obtained by the desulfonation procedure.



An independent synthesis of III was accomplished *via* 2-benzyl-4,6-dimethylaniline (IV) obtained by the action of aluminum chloride on N-benzyl-2,4-dimethylaniline. Similar isomerizations of a number of N-alkylanilines at elevated temperatures under the influence of hydrohalic acids or Lewis acids have been studied by Hickinbottom, *et al.*,[4] and Davies, *et al.*,[5] have reported the analogous preparation of 2-benzyl-4-methylaniline by treatment of N-benzyl-*p*-toluidine with *p*-toluidine and aluminum chloride. Replacement of the $-NH_2$ group of IV with $-SO_2H$ by diazotization in 30% sulfuric acid and treatment with sulfur dioxide and copper gave III.



The deep red color of the *n*-butyllithium–sulfone reaction mixture which fades as the reaction proceeds is consistent with the intermediate II, which should be appreciably ionic in view of possible resonance structures such as V.[6]



Since metalation of toluene with organolithium compounds[7] gives only very low yields of benzyllithium, and since in the reaction of *n*-butyllithium with phenyl *p*-tolyl sulfone[3b] as well as with mesityl phenyl sulfone[8] no evidence of metalation at the *p*-methyl group was obtained, the completeness of our reaction must be due to the presence of the sulfone grouping *ortho* to the methyl group. It would seem that neither the possible enhancement of the acidity of the hydrogens of the *o*-methyl group due to hyperconjugation with the sulfone group, nor stabilization of the resulting carbanion by conjugation with the sulfone group, can explain the facile formation of II[9] by direct metalation, since these effects would also apply to the *p*-methyl group.

The concept of a nucleophilic attack by the organometallic has been used to explain the nuclear metalation of substituted benzenes.[10] Such an explanation emphasizes the enhanced acidity of the *o*-hydrogens due to inductive and field effects of substituents such as fluoro, trifluoromethyl or methoxyl groups. Possibly the inductive effect of the sulfone group at least partially accounts for our observations, although it is problematical whether such an effect would have a marked bearing on the acidity of the hydrogens of the *o*-methyl group, which are separated by three carbon atoms from the activating sulfone group. Although a precise explanation of the metalation step is beyond the scope of this paper, it might be suggested that the spatial proximity of the oxygens of the sulfone group to the hydrogens of the *o*-methyl group and possible complexation of *n*-butyllithium at the sulfone group[3a] are important factors in facilitating metalation at an *o*-methyl group.

Further evidence for the proposed rearrangement mechanism was obtained by studying the rearrangement of mesityl *p*-tolyl sulfone. The *p*-tolyl configuration was maintained in the product, indicating that, as in the Smiles rearrangement,[2] our rearrangement occurs by displacement of the arylsulfonyl group at the position to which it was originally attached in the starting sulfone and not at a position *ortho* to this attachment, as in the Sommelet rearrangement.[11]

It is interesting to note that while the reaction of mesityl phenyl sulfone (I) with an equimolecular amount of *n*-butyllithium gave an almost quanti-

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(4) J. Reilly and W. J. Hickinbottom, *J. Chem. Soc.*, **117**, 103 (1920); W. J. Hickinbottom, *ibid.*, **124**, 64 (1927); W. J. Hickinbottom and A. C. Waine, *ibid.*, 1558 (1930); W. J. Hickinbottom and G. H. Preston, *ibid.*, 1566 (1930); W. J. Hickinbottom, *ibid.*, 1119 (1937).

(5) R. E. Davies, H. T. Openshaw, F. S. Spring, R. H. Stanley and A. R. Todd, *ibid.*, 295 (1948).

(6) *o*-Methyl substituents do not appear to hinder conjugation on the part of a sulfone group; H. Kloosterziel and H. J. Backer, *Rec. trav. chim.*, **72**, 185 (1953).

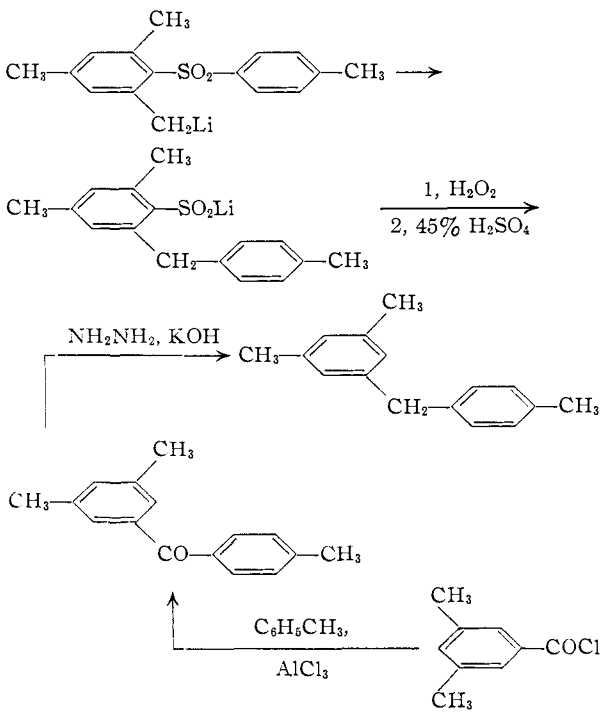
(7) H. Gilman, H. A. Pacevitz and O. Baine, This Journal, **62**, 1514 (1940).

(8) We have found that the rate of rearrangement of mesityl phenyl sulfone and phenyl 2,6-xylyl sulfone is the same within experimental error. This minimizes the possibility of initial metalation at the *p*-methyl group followed by transfer of the metal from the *p*- to the *o*-methyl group.

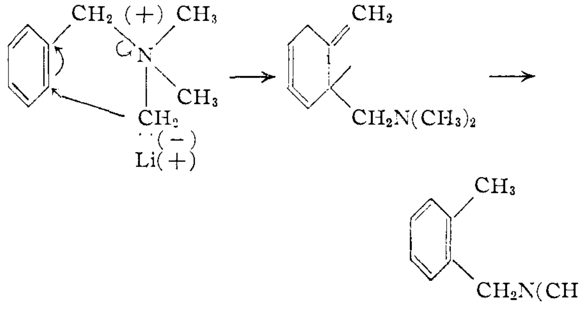
(9) As will be seen in a later paper, the metalation of I in refluxing ether is very rapid.

(10) D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954); G. E. Hall, R. Piccolini and J. D. Roberts, This Journal, **77**, 4540 (1955).

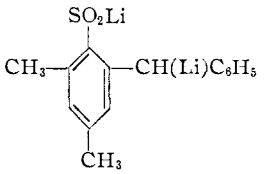
(11) S. W. Kantor and C. R. Hauser, *ibid.*, **73**, 4122 (1951), have given evidence in support of the following mechanism for the Sommelet rearrangement.



tative yield of III, when the amount of metalating agent was increased to twice that of the sulfone, the yield dropped to 46%, the remainder of the reaction mixture being a neutral oil.

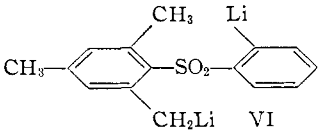


That this oil was not the result of a reaction between the product (salt of III) and excess *n*-butyllithium was established by refluxing an ether suspension of the lithium salt of III with an equimolecular amount of the metalating agent. The salt dissolved rapidly to give an intensely red colored solution which, after the usual reaction time, resulted in a 98% recovery of III, on hydrolysis and acidification. That the lithium arenesulfinate dissolved to give a colored solution suggests that the reactant was metalated, presumably to give



The neutral oil later was shown to contain approximately 40% of the starting mesityl phenyl sulfone by infrared analysis. Part of the sulfone was subsequently recovered *via* vacuum distillation, although the majority of the oil resinified during the process.

If the metalation of I to give II is rapid (as will be shown in a later paper), followed by a slower rearrangement, it seems possible that in the presence of excess *n*-butyllithium, II might be metalated again to give VI. This species would


VI

probably not undergo rearrangement due to the proximity of the negative end of the carbon–lithium dipole in the phenyl ring to the carbon atom at which nucleophilic attack must occur if rearrangement is to take place.[12] On hydrolysis, VI would, of course, give rise to mesityl phenyl sulfone. Since the metalation of II to give VI must compete with the rearrangement of II, and since the product contained approximately equal amounts of the starting mesityl phenyl sulfone and of III, these two reactions must occur at similar rates.

Experimental[13]

Mesityl Phenyl Sulfone.—A well-stirred solution of 100 g. (0.83 mole) of mesitylene and 116 g. (0.66 mole) of benzenesulfonyl chloride in 400 ml. of carbon disulfide was treated with 100 g. (0.75 mole) of aluminum chloride in small amounts over a period of 0.5 hour. After 5 hours of reflux the mixture was hydrolyzed with hydrochloric acid and ice. The organic layer was separated with the aid of benzene, washed once with water and once with dilute ammonia, filtered and dried. After removing the solvent, the product boiled at 150–170° (0.3 mm.), and solidified in the receivers. The light yellow solid weighed 124 g. (72%) and melted at 80–80.5° after crystallization from methanol; reported[14] m.p. 116°.

Anal. Calcd. for $C_{15}H_{16}O_2S$: C, 69.21; H, 6.20. Found: C, 69.36; H, 6.34.

This product was identical with that obtained by the Friedel–Crafts reaction of mesitylenesulfonyl chloride with benzene, but its melting point was much lower than that reported by Meyer.[14] Meyer prepared his sulfone by the action of mesitylenesulfonic acid on benzene using the same procedure that he employed in the preparation of a number of other sulfones. The melting points of most of Meyer's sulfones compare quite favorably with the melting points reported by other workers. The following sulfones, all of which have been prepared in this Laboratory, are exceptions, however. Our melting points for phenyl *p*-tolyl sulfone[16] and dimesityl sulfone[17] are substantiated in the literature.

TABLE I

Sulfone	Our m.p., °C.	Meyer's m.p., °C.
Mesityl phenyl	80 - 80.5	116
Phenyl *p*-tolyl	125 -126	80
Mesityl 2,4-xylyl[15]	156 -157.5	149
Dimesityl	203.5–205	195

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[12] As in the Smiles rearrangement (see ref. 2), the charge induced by the sulfone grouping at the site of the prospective nucleophilic displacement must play an important role in facilitating rearrangement. Any group, therefore, which reduces the magnitude of this charge at the carbon atom in question will hinder or even prevent rearrangement.

[13] All melting and boiling points are uncorrected.

[14] H. Meyer, *Ann.*, **433**, 327 (1923).

[15] Prepared by the oxidation of the corresponding sulfide from the reaction of mesitylmagnesium bromide on 2,4-dimethylbenzenesulfenyl chloride.

[16] E. Bourgeois, *Ber.*, **28**, 2323 (1895).

[17] M. E. Maclean and R. Adams, THIS JOURNAL, **55**, 4685 (1933).

It may be suggested that the melting point of mesityl phenyl sulfone was mistakenly recorded for that of phenyl *p*-tolyl sulfone in Meyer's paper and *vice versa*. The latter sulfone was well known[16] at the time Meyer published his results and it seems improbable that he overlooked a difference of 45° between the melting point of his sulfone and the value reported in the literature. Indeed, he actually remarked that, "The behavior of this compound complies entirely with the description in the literature."[14] Although this reasoning leads to a melting point of Meyer's phenyl *p*-tolyl sulfone that is still about 8° too low, the commonly reported[16] melting point being 124–125°, the melting points of Meyer's dimesityl and mesityl 2,4-xylyl sulfones are also about 8° too low.

The Reaction of Mesityl Phenyl Sulfone (I) with *n*-Butyllithium.—In a typical run, a well-stirred solution of 2.00 g. (0.0077 mole) of mesityl phenyl sulfone in 100 ml. of anhydrous ether was brought to reflux and treated rapidly with a 1.03 molar solution containing 0.0081 mole of the organometallic.[18] After 2 hours of reflux, the solution was hydrolyzed with 100 ml. of water and the layers separated. Acidification of the water layer with hydrochloric acid, and extraction with ether followed by evaporation of the solvent gave 1.96 g. (98%) of an almost colorless solid.

Purification was accomplished by dissolving in 100 ml. of aqueous sodium bicarbonate and shaking with charcoal until colorless. Isolation from the basic solution as before followed by crystallization, carried out by dissolving in acetone at 40°, adding water until precipitation began and cooling, gave a colorless solid, m.p. 92.5–94.7° dec.; neut. equiv. calcd. for 2-benzyl-4,6-dimethylbenzenesulfinic acid (III), 260.3; found 260.7. Mixed melting points with an authentic sample of this acid (below) showed no depression.

The Reaction of a Twofold Excess of *n*-Butyllithium with Mesityl Phenyl Sulfone (I).—A solution of 8.32 g. (0.0320 mole) of mesityl phenyl sulfone (I) in 500 ml. of ether was brought to reflux and treated rapidly with 0.064 mole of *n*-butyllithium.[18] After 1.5 hours of reflux, the reaction mixture was hydrolyzed and the sulfinic acid isolated as above, weight 3.78 g. (46%). The neutral equivalent of the crude acid was 279, the calculated value being 260.[19]

Evaporation of the solvent from the neutral ether fraction of the reaction mixture gave 5.52 g. of a light yellow oil which refused to crystallize. The infrared spectrum of this oil contained all the absorption bands characteristic of mesityl phenyl sulfone. When the infrared spectrum of this oil (3.00 g./10 ml. of carbon tetrachloride solution) was run using a solution of mesityl phenyl sulfone (1.80 g./10 ml. of solution) in the reference cell, the base line was almost straight throughout the spectrum. The oil, therefore, was about 60% mesityl phenyl sulfone, accounting for 40% of the starting sulfone.

Distillation of the oil from a similar run employing 26 g. (0.10 mole) of the sulfone was carried out at 0.2 mm. Only a few drops of the distillate came over below 160°, the approximate boiling point of mesityl phenyl sulfone, while almost 8 g. of material distilled at 160–180°. From this fraction several grams of mesityl phenyl sulfone was recovered. The cooled pot residue was a dark, brittle resin.

The Reaction of *n*-Butyllithium with the Lithium Salt of III.—A solution of 1.00 g. (0.00385 mole) of the carefully purified sulfinic acid III in 25 ml. of ether was treated dropwise with 0.00385 mole of *n*-butyllithium[18] in about 25 ml. of ether. The suspension of the lithium salt of III so formed was brought to reflux and treated with a second equimolar amount of metalating agent. The lithium arenesulfinate dissolved rapidly to give an intensely red colored solution. After 1.5 hours of reflux the sulfinic acid was recovered as described above, weight 0.98 g. (98% recovery).

Oxidation and Desulfonation of the Product from the Metalation of Mesityl Phenyl Sulfone (I).—A solution of 2.5 g. (0.0096 mole) of the acid, from the reaction of I with *n*-butyllithium, in 30 ml. of aqueous sodium bicarbonate was treated with 3 ml. of 30% hydrogen peroxide. After standing overnight, the solution was evaporated to near dryness. The residue was dissolved in 29 ml. of water, acidified with concentrated sulfuric acid and treated with another portion of concentrated sulfuric acid weighing 25 g. After 3 hours of reflux and standing on the steam-bath for 7 hours, the mixture was diluted with water and extracted with ether. The ether solution was washed with water, dried, and the solvent boiled off. The product distilled at 120–122° (2 mm.), and weighed 1.47 g. (83% of theory), n^{23}D 1.5651. The refractive index of an authentic sample of 3,5-dimethyldiphenylmethane (below) was 1.5656 at 23°.

3,5-Dimethylbenzophenone.—A solution of 51.8 g. (0.307 mole) of 3,5-dimethylbenzoyl chloride in 66.5 ml. (58.5 g., 0.750 mole) of benzene was treated with 45.0 g. (0.338 mole) of aluminum chloride in small portions over a period of 25 minutes. Refluxing was maintained for 1.5 hours after which the solution was hydrolyzed with ice and hydrochloric acid. The resulting mixture was boiled gently until the odor of benzene had disappeared and the resulting red oil was taken up in ether. After being washed with water, the ether solution was dried and the solvent distilled off. The product distilled at 155–157° (4 mm.), weighed 57.6 g. (89%) and melted at 68–69° on crystallization from aqueous methanol (reported[20] m.p. 70°).

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 86.01; H, 6.93.

3,5-Dimethyldiphenylmethane.—The above ketone was reduced according to the method of Huang-Minlon[21] using sodium hydroxide, 85% hydrazine hydrate, diethylene glycol and 21 g. (0.10 mole) of ketone. Vacuum distillation of the product gave 15.4 g. (79%) of a hydrocarbon, b.p. 121–122° (2.5 mm.), n^{23}D 1.5656.

Anal. Calcd. for $C_{15}H_{16}$: C, 91.77; H, 8.22. Found: C, 92.09; H, 8.11.

N-Benzyl-2,4-dimethylaniline.—Using a procedure similar to that described by Davies, *et al.*,[6] 43 g. (0.34 mole) of benzyl chloride was added dropwise over a period of 1.5 hours to a well-stirred mixture of 161 g. (1.3 moles) of 2,4-dimethylaniline, 35 g. of sodium bicarbonate and 33 ml. of water maintained at 90–95°. Heating was continued for 0.5 hour after the addition was complete. The resulting mixture was filtered while hot and the oily layer separated. After being washed once with a saturated salt solution, the oil was dried with magnesium sulfate. The excess 2,4-dimethylaniline was distilled off at 10 mm. The yellow oil distilled at 116–121° (0.2 mm.) and weighed 55 g. (77%). This oil was used below without further purification.

2-Benzyl-4,6-dimethylaniline.—Using the method of Davies, *et al.*,[5] 55 g. (0.26 mole) of the above N-benzyl-2,4-dimethylaniline together with 55 g. (0.45 mole) of 2,4-dimethylaniline was treated with 13 g. (0.098 mole) of aluminum chloride at 200°, heating and stirring being maintained for 22.5 hours. After being cooled, the mixture was poured into excess base. The layers were filtered and the organic layer separated and dried after the addition of a little ether. After distillation of the 2,4-dimethylaniline at 10 mm., the product boiling at 118–145° (0.2 mm.) was collected. A second distillation gave 28 g. (50%) of a yellow oil, b.p. 128–131°.

Conversion of 23 g. of this oil to the acetyl derivative and crystallization from toluene gave 10 g. of a white solid, m.p. 160–161.5°. Hydrolysis of 8 g. of the acetanilide was accomplished by boiling with 1:1 hydrochloric acid for 3 days with enough added ethanol to cause solution. At the end of this time, a sample of the hydrolysis mixture diazotized cleanly and the resulting diazonium salt coupled readily with β-naphthol.

The hydrolysis mixture was basified and extracted with ether. Evaporation of the solvent gave 5.5 g. (approx. 15% over-all) of an almost colorless, crystalline amine, which was used below without further purification.

2-Benzyl-4,6-dimethylbenzenesulfinic Acid.—Using the method of Gattermann,[22] a solution of 5.0 g. (0.024 mole) of the above 2-benzyl-4,6-dimethylaniline in 100 g. of warm, 30% sulfuric acid was cooled to 0° and diazotized with 3.4 g. (0.049 mole) of sodium nitrite in 20 ml. of water. To the resulting solution was added 25 g. of cold, 60% sulfuric acid. Sulfur dioxide was bubbled in while the solution was maintained at −5°, the addition being quite slow until the

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[18] The *n*-butyllithium was prepared and titrated according to the method described by R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 339.

[19] Due to the instability of this and similar sulfinic acids, thorough drying of the unpurified acid gave rise to base-insoluble products which considerably increased the neutral equivalent.

[20] G. Baddeley, *J. Chem. Soc.*, 235 (1944).

[21] Huang-Minlon, This Journal, **68**, 2487 (1946).

[22] L. Gattermann, *Ber.*, **32**, 1136 (1899); M. E. Hanke, This Journal, **45**, 1321 (1923).

initial evolution of the oxides of nitrogen subsided. The addition was continued until the gain in weight of the solution was 30 g. The coolant was then removed and the solution allowed to warm slowly to 15° with the addition of small amounts of copper bronze from time to time. Vigorous stirring was maintained throughout. The solution was filtered and the sulfinic acid dissolved in base. After removal of unreacted copper, the solution was acidified and extracted with ether which was in turn extracted with aqueous sodium bicarbonate. The bicarbonate solution was shaken with charcoal, acidified and the product isolated with ether, 1.1 g. (22%) being obtained. The low yield here is somewhat surprising in view of the much higher yields obtained in this Laboratory from the conversion of similar anilines to the corresponding sulfinic acids. Such anilines, however, differed from 2-benzyl-4,6-dimethylaniline in having only a single *o*-substituent, while the latter is substituted in both the 2- and 6-positions. The decomposition of its diazonium salt may, therefore, occur at appreciably higher temperatures than those required for similar amines with only a single *o*-substituent.

After crystallization from aqueous acetone as above, the acid melted at 92.7–94.7° dec. and had a neutral equivalent of 263.0; calculated for 2-benzyl-4,6-dimethylbenzenesulfinic acid is 260.3.

The Reaction of Mesityl *p*-Tolyl Sulfone with *n*-Butyllithium.—A solution of 24.7 g. (0.090 mole) of mesityl *p*-tolyl sulfone in 600 ml. of ether at 0° was treated, over a period of 15 minutes, with a solution of *n*-butyllithium from 1.61 g. (0.23 g. atom) of lithium wire and 15.5 g. (0.113 mole) of *n*-butyl bromide in 135 ml. of ether. Assuming an 80% yield of the organometallic, 0.09 mole of *n*-butyllithium was added.

After stirring for 1.5 hours at 0°, the reaction mixture was allowed to warm to room temperature and stand overnight. Hydrolysis with 100 ml. of 3 *N* hydrochloric acid was followed by separation and extraction of the ether layer with two 75-ml. portions of 8% sodium hydroxide and one 75-ml. portion of water. The washings were combined and acidified to give an oil which crystallized almost immediately. Solution of this acid in methanol and treatment with charcoal followed by crystallization, after adding water, gave 18.8 g. (76% of theory) of colorless needles, m.p. 90–91° dec. The neutral equivalent of this acid was 278; calcd. for 2-(4-methylbenzyl)-4,6-dimethylbenzenesulfinic acid, 274.

2-Chloromercuri-3,4′,5-trimethyldiphenylmethane.—Using the procedure described by Whitmore, *et al.*,[23] the chloromercuri derivative was prepared from 1.00 g. (0.00368 mole) of the sodium salt of 2-(4-methylbenzyl)-4,6-dimethylbenzenesulfinic acid and 1.00 g. (0.00365 mole) of mercuric chloride. Crystallization of the product from aqueous alcohol gave fine white needles, weight 0.71 g. (44% of theory), m.p. 132–133°.

Anal. Calcd. for $C_{16}H_{17}HgCl$: Cl, 7.96. Found: Cl, 7.96.

Oxidation and Desulfonation of the Reaction Product of Mesityl *p*-Tolyl Sulfone and *n*-Butyllithium.—This process was carried out in the same manner as described above for the oxidation and desulfonation of the rearrangement product of mesityl phenyl sulfone, using a 7.0-g. (0.026 mole) sample of the sulfinic acid. The product weighed 2.34 g. (43%) and boiled at 130–131° (4 mm.), $n^{20.5}D$ 1.5613. The refractive index of 3,4′,5-trimethyldiphenylmethane (below) is 1.5611 at 21°.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.52; H, 8.87.

3,4′,5-Trimethylbenzophenone was prepared from 14.1 g. (0.084 mole) of 3,5-dimethylbenzoyl chloride, 18.8 g. (0.204 mole) of toluene and 12.3 g. (0.092 mole) of aluminum chloride in the manner described above for the preparation of 3,5-dimethylbenzophenone. After vacuum distillation, the yellow solid was purified by low-temperature crystallization from methanol. The fine white crystals so obtained melted at 75.0–75.5°, 12.9 g. (68%) being obtained.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.75; H, 7.19. Found: C, 85.84; H, 7.40.

3,4′,5-Trimethyldiphenylmethane.—The above 3,4′,5-trimethylbenzophenone was reduced by the Wolff–Kishner method as modified by Huang-Minlon[19] using sodium hydroxide, 85% hydrazine hydrate, diethylene glycol and 8.9 g. (0.040 mole) of the ketone. Vacuum distillation of the product at 110–115° (1 mm.) gave a hydrocarbon, $n^{21}D$ 1.5611.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.44; H, 8.52.

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LAFAYETTE, INDIANA

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[23] F. C. Whitmore, F. H. Hamilton and N. Thurman, THIS JOURNAL, **45**, 1066 (1923).

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Chemistry of Enolates. II. Self-condensation of Methyl Trityl Ketone. A Novel Claisen Condensation

BY JANICE L. GREENE[1] AND HARRY D. ZOOK

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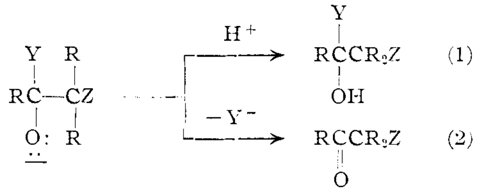
β-Diketones have been prepared by acylation of the sodium enolate of methyl trityl ketone. Acylation by the ketone itself results in a Claisen-type condensation in which the condensate anion is converted to the β-diketone by elimination of triphenylmethide ion. An improved preparation for methyl trityl ketone and the instability of this ketone in sulfuric acid are described.

Base-induced condensations of carbonyl compounds give condensate anions which may be stabilized by either of two paths: (1) extraction of a proton from the solvent (aldol condensation) or (2) elimination of a stable anion (Claisen condensation).



$$\underset{\underline{\ddot{O}}:}{\overset{Y}{RC}}\text{—}\underset{R}{\overset{R}{CZ}} \begin{cases} \xrightarrow{H^+} \mathrm{R}\underset{OH}{\overset{Y}{C}}\mathrm{CR_2Z} & (1) \\ \xrightarrow{-Y^-} \mathrm{R}\underset{\| \atop O}{C}\mathrm{CR_2Z} & (2) \end{cases}$$

The latter reaction is familiar in the condensa-

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[1] This paper forms part of a Ph.D. thesis by Janice L. Greene, Allied Chemical and Dye Corporation Fellow, The Pennsylvania State University, 1954–1955.